WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

WO 94/22313 (51) International Patent Classification 5: (11) International Publication Number: A1 A21D 8/08, A23D 7/00, 7/02 (43) International Publication Date: 13 October 1994 (13.10.94) (81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CN, (21) International Application Number: PCT/AU94/00155 CZ, DE, DK, ES, FI, GB, GE, HU, JP, KG, KP, KR, KZ, LK, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, 31 March 1994 (31.03.94) (22) International Filing Date: RO, RU, SD, SE, SI, SK, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, (36) Priority Data: GA, GN, ML, MR, NE, SN, TD, TG). 1 April 1993 (01.04.93) ΑŪ PL 8105 **Published** (71) Applicant (for all designated States except US): ICI AUS-With international search report. TRALIA OPERATIONS PROPRIETARY LIMITED [AU/AU]; 1 Nicholson Street, Melbourne, VIC 3000 (AU). (72) Investor; and (75) Investor/Applicant (for US only): MEEKER, Frederick, John [AU/AU]; Parker's Road, Russell's Bridge, VIC 3331 (AU). (74) Agent: DAVY, John, R.; Industrial Property Section, ICI Australia Operations Proprietary Limited, 1 Nicholson Street, P.O. Box 4311, Melbourne, VIC 3001 (AU).

(54) Title: PAN RELEASE AGENT

(57) Abstract

A fluid pan release agent comprising an emulsion comprising at least one oil, an aqueous phase and at least one emulsifier which agent can be applied to baking pans to facilitate ease of product release from the baking pan. Preferably the pan release agent exhibits non-Newtonian flow characteristics or more preferably Bingham plastic flow and thixotropic flow characteristics.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

ፈ ⋅

	• 	GB	United Kingdom	MIR	Macritania
AT	Austria	GE	Georgia	MW	Malawi
ΑŪ	Address	GN	Guinea	NE	Niger
33	Barbados		Greece	NL	Netherlands
BE	Belgium	GR		NO	Norway
BF	Burkina Faso	HU	Hungary	NZ	New Zealand
BG	Bulgaria	Œ	Ireland		Poland
BJ	Benin	п	Italy	PL.	· ·
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgystan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic	SD	Sudan
_			of Korea	SE	Sweden
CG	Congo	KR	Republic of Korea	SI	Slovenia
CB	Switzerland	KZ	Kazakhstan	SIK	Slovakia
a	Côte d'Ivoire	ü	Liechtenstein	SN	Senegal
CM	Cameroon		Sri Lanka	TD	Chad
CN	China	LK		TG	Togo
cs	Czechoslovakia	LU	Luxembourg	ŢĴ	Tajikistan
cz	Czech Republic	LV	Latvia	Π	Trimidad and Tobego
DE	Germany	MC	Monaco	UA.	Ukraine
DK	Denmark	MD	Republic of Moldova	_	United States of America
ES	Spain	MG	Madagascar	US	
n	Finland	. MIL	Mali	UZ	Uzbekistan
FR	Prance	MN	Mongolia	VN	Viet Nam
F.M.	Cohen				

PAN RELEASE AGENT

The current invention relates to baking pan release agents which facilitate ease of product release from the baking pan and avoid the build up of carbon residue on the pan surface and the method of use of such agents. The pan release agent of the current invention is particularly effective on baking pans used for dough products, including yeast products such as bread.

5

10

15

20

25

Pans for baking dough products such as bread are generally constructed of steel coated with aluminium, tin or similar metal. Dough products baked in such a pan will not generally release cleanly unless the inside of the pan is coated in some manner. It is a requirement of the baking industry in general that bread rolls and loaves be cleanly de-panned using commercial methods. If a baked dough product such as a loaf of bread sticks to the pan then excessive time and effort may need to be spent liberating the loaf and subsequently cleaning off pieces of crust which adhere to the pan. A damaged dough product is generally discarded as the baking industry requires that baked dough products have an attractive appearance and are not damaged or marked due to the baking process.

A traditional approach has been the use of metal surfaces which are preconditioned by treatment with vegetable oil which, when subjected to high temperatures in the baking oven, produces a conditioned surface from which dough products can be released using release agents of the prior art.

Another approach to achieving clean release of baked dough products from pans is to glaze the inside of the pans with a silicon polymer. The glaze is usually a silicone emulsion based on dimethyl phenyl siloxane monomers which form a thin, semi-permanent polymer coat on the inside of the dough pan. Such silicone coatings are normally applied to newly manufactured bread pans before their purchase by bakers.

However, the high temperatures used in the baking process and high humidity

10

15

20

25

30

tends to cause hydrolysis of the silicon polymer coating the pan and eventually all the organic components of the polym r decompose, I aving a matrix of silicon dioxide. After about 400 baking cycles the dough pan starts to form a brown scale, starts to show a significant deterioration in appearance and the baked product starts to stick.

Most dough pans coated with a silicone based polymer have to be reconditioned periodically by chemical stripping followed by recoating. Bread pans for example, are routinely used for about 24 months at 20 baking cycles per week before the baker must pay to have them reconditioned and reglazed. By comparison, glazed roll trays can be used for up to 3 years before reglazing Such reconditioning is expensive and the bakery has to invest in additional pans while a proportion of their pans are being reglazed.

To overcome the relatively short release life of silicon polymer coatings, the interior of baking pans are often sprayed with a pan release agent prior to each baking cycle. These release agents provide a film between the dough and the coated (or uncoated) metal of the pan and thus effects release.

Problems are created by the use of pan release agents of the prior art such as neat vegetable oil and water-in-oil emulsions such as TINCOL. (TINCOL is a registered trade mark of Australian Bakels Pty Ltd.) Pan release agents of the prior art suffer from the build up of polymerised, organic material which is primarily composed of residual pan release agent mixed with entrained extraneous material and the baking temperatures of 200 to 300°C causes them to oxidise or burn and leave a black carbon residue. The resultant carbon residues tend to initially build up on areas which do not contact the dough but eventually migrate to contact areas, causing the baked product to stick to the pan, leaving black marks on the crusts of baked dough. Oversprayed pan release agents of the prior art also tend to build up on the outside of the pans and become sticky, collecting starch dust, crumbs and other dry materials which eventually polymerise to form a permanent deposit which interferes with heat transfer from the oven to baking dough. The build up is usually removed

10

15

20

25

30

only when the pan is chemically stripped prior to reglazing.

Wat r based pan rel ase agents of the prior art are generally oil-in-water emulsions which comprise a major proportion of water and less than 10% w/w oil. Typical water based pan release agents of the prior art are described in U.S. Patent no.s 4,547,388 and 4,339,465 and were primarily developed to overcome the mess associated with earlier oil based products. However, these products eventually suffer the drawback of polymerisation under bakery conditions and while they are effective on horizontal surfaces, they do not adhere adequately enough to the vertical sides of dough pans to make them effective pan release agents.

In the past, efforts have been made to improve the adherence of pan release agents to the sides of pans by adding lecithin however this additive suffers the drawback forming a char on the pan when heated. Some pan release agents which adhere well to the vertical sides of dough pans can only exhibit this type of rheology in the absence of preservatives. As a result their shelf life does not extend further than a few days, making them impractical for use in commercial food manufacture. Furthermore some pan release agents of the prior art which exhibit good adherence to pan walls in their neat form show poor adherence in their diluted form - dilution being necessary to provide a solution of low enough viscosity that it can be sprayed onto dough product pans.

As spraying is the preferred commercial method of applying pan release agents to dough product pans, the pan release agents used must be capable of even spray distribution at normal operating pressures of conventional spray pumps. Water based pan release agents are generally of low viscosity, however this low viscosity presents some inconvenient flow properties when sprayed on the vertical sides of dough pans. Water based pan release agents of the prior art exhibit flow characteristics which tend to cause them to flow down the sides of the pan, flooding the pan base and leading to sticking of the baked product at the sides. Such pan release agents are limited in use to flat surfac s such as trays.

10

15

20

25

30

The pr blems associated with the pan rel ase ag nts of the prior art can now be alleviated by the pan r l ase agent of the current inv ntion and its method of use.

The present invention provides a fluid pan release agent comprising an emulsion comprising at least one oil, an aqueous phase and at least one emulsifier, wherein the mass ratio of aqueous phase:oil:emulsifier is from 75 to 90 for the aqueous phase, from 3 to 10 for the oil phase and from 1 to 12 for the emulsifier. Preferably the pan release agent of the present invention may exhibits non-Newtonian flow characteristics. More preferably the pan-release agent of the invention exhibits Bingham plastic flow and thixotropic flow characteristics. In a further preferment the pan release agent of the present invention exhibits flow characteristics which permit it to flow readily under applied pressure but which restricts its flow at atmospheric pressure.

In a further preferred embodiment the current invention provides a pan release agent which is water dispersable and has non-Newtonian flow properties which permits the pan release agent to be sprayed at low pressures yet achieve adequate adhesion to the vertical walls of dough product pans.

Fluids can be generally categorised by their flow response. Most fluids are Newtonian fluids in which at a given temperature the shear stress is proportional to shear rate. In a further embodiment the invention provides a fluid pan release agent comprising at least one oil, an aqueous phase and at least one emulsifier wherein said fluid agent exhibits non-Newtonian flow characteristics. Some fluids exhibit non-Newtonian behaviour including plastic flow, dilatant flow, pseudoplastic flow, thixotropic flow and Bingham plastic flow. Bingham plastic fluids differ from Newtonian fluids in that they require minimum shear rate to induce a sudden and rapid decrease in viscosity. Thixotropic fluids exhibit a measurable decrease in viscosity with increased shear rate and most importantly a recovery of viscosity when shear rate is reduced and/or removed. In yet a further embodiment the invention provides a fluid pan release agent comprising at least one oil, an aqueous phase and at least one emulsifier

10

15

20

25

wherein said fluid agent xhibits Bingham plastic flow and thixotropic flow characteristics.

It is preferred that the pan release agents of the present invention exhibit Bingham plastic flow and thixotropic characteristics as these characteristics result in a pan release agent which flows readily under reduced pressure and may be sprayed like a thin oil using standard spraying equipment operating at 1 to 3 bars. Furthermore, once the pressure is removed the agent adheres to the vertical sides of dough pans on which it has been sprayed and does not run. Without wishing to be bound by theory it is speculated that the pan release agent of the current invention may comprise a double emulsion such as a water-in-oil emulsion component in an oil-in-water emulsion.

The Bingham plastic flow properties of an emulsion is dependent on the proportions of water, oil and emulsifier in the composition. In a particular preferment of the pan release agent of the present invention, the mass ratio of aqueous phase:oil:emulsifier is from 85 to 90 for the aqueous phase, from 3 to 7 for the oil phase and from 5 to 10 for the emulsifier.

The aforementioned flow characteristics significantly affect the ease of application of pan release agents to dough pans. The pan release agent of the current invention can be sprayed like a thin oil onto dough pans using relativ ly low pressure. Conversely, the oil based pan release agents of the prior art require significantly higher pressures for spray application to dough pans.

A further significant advantage of the pan release agent of the current invention is its water dispersability. When heated, repeated applications of pan release agents of the current invention causes formation of a soft polymeric film on the metal or coating of the dough pan which can be washed off using hot water. Conversely the oil based pan release agents of the prior art form a very hard, polymeric lay r which cannot be removed using hot water alone.

Emulsifi rs suitable for use in the composition of the current invention include

10

15

20

mulsifi rs included in th Australian Foods Standards code of the thos National Food Authority. Many other suitable emulsifiers not included in this cod will be apparent to the person skilled in the art. Examples of such emulsifiers include mono-glycerides and di-glycerides of fat forming fatty acids and monostearates such as polyoxyethylene(20) sorbitan mono-stearate (which is commonly known as polysorbate), sorbitan mono-stearate and other monostearates, mono-oleate derivatives and mixtures thereof. It is generally known in the trade that emulsions of adequate stability for use in foodstuffs are obtained by using at least two emulsifiers of widely differing HLB value. In a preferred embodiment the pan release agent of the current invention comprises similar quantities of glycerol mono-oleate, sorbitan mono stearate and polyoxyethylene sorbitan mono-stearate. In another preferred embodiment the pan release agent of the current invention comprises similar quantities of glycerol mono-stearate, sorbitan mono-stearate and polyoxyethylene monooleate.

In a preferred embodiment the oil phase of the pan release agent of the current invention comprises one or more liquid vegetable oils or animal fats suitable for use in foodstuffs. Oils such as canola oil, sunflower oil, soya oil or palm oil ar suitable and many other oils will be apparent to those skilled in the art. In a preferred embodiment the pan release agent comprises between 3% w/w and 10% w/w of oil phase.

The aqueous phase of the pan release agent of the current invention comprises greater than 75% w/w of water. The proportion of continuous aqueous phase includes any water present in the emulsifier.

In a preferred embodiment the pan release agent of the current invention can be removed from surfaces by application of water. Without wishing to be bound by theory it is suggested that the large proportion of water present in the formulation of the pan r lease agent of the current invention and the compositional parameters of the current invention provide a pan release agent which can be readily removed from a sprayed pan by washing with water

10

15

alone. This is a significant benefit and advantage in keeping dough pans clean and free of pan r I ase agent buildup and subsequent build up with associated mess.

It will be apparent to the person skilled in the art that certain additives are advisable and/or required by law in dough based foodstuffs to improve certain properties such as resistance to oxidation and mould resistance. Additives such as sorbic acid, acetic acid, phosphoric acid, benzoic acid and propionic acid are commonly used in foodstuffs and may be added as a preservative in the pan release agents. In a preferred embodiment the pan release agent of the current invention comprises at least one preservative.

It will be apparent to the person skilled in the art that the pan release agent of the current invention may be applied to a pan and/or dough in many ways but is preferably sprayed onto the pan before the dough is placed in it or sprayed onto the dough after being placed in the pan but before proofing. The pan release may provide additional benefits such as aiding the adhesion of poppy seeds, sesame seeds or other seeds or matter to the top of the dough. The pan release agent of the current invention may be used both on dough pans which do not have a baked on coating such as silicon polymers as well as pans which do have such a coating.

EXAMPLE 1

A pan release ag nt was prepared from th following compon nts;

-	Component Pro	Proportion	
1	Glycerol Mono Oleate (GMO)	2.0 %	
1	SPAN-60 (Sorbitan Mono Stearate)	3.0%	
	TWEEN-60 (Polyoxyethylene Mono Stearate) 2.0%	
1	Canola Oil	4.0%	
1	Water	88.5%	
	Sorbic Acid	0.25%	
1	Acetic Acid	0.25%	

20

25

30

The GMO, canola oil, SPAN-60 and TWEEN-60 were combined and heated to 80°C and stirred until homogeneous. (SPAN and TWEEN are registered trade marks of ICI Americas Inc.) The non-aqueous phase was then poured in a thin stream into the stirred aqueous phase at 20°C such that immediate dispersion occurred. The food acids were then dissolved in a minimum amount of water and added to the emulsion which was then stirred until homogeneous.

The fluid pan release agent so formed was stored in a polylined steel drum which was connected to an air pump. The air pump was then operated at a constant fluid pressure of 2 bar and the pan release agent evenly sprayed over the inner walls and base of several glazed bread pans and several unglazed pans. The same pans were used for 400 baking cycles and resprayed with pan release agent before each cycle. In all cases there was optimal depanning of the baked loaf with no build up of carbonised residue.

10

EXAMPLE 2

The flow characteristics of the pan release agent Example 1 were measured and compared with equivalent characteristics of a pan release agent of the prior art known as TINCOL. Graph 1 is a graph of the log of the shear rate (1/s) versus shear stress (Pascal) and Graph 2 is a graph of viscosity (Pascal.sec.) versus shear stress (Pascal) imposed upon the two samples.

Graph 1 shows that the pan release agent of Example 1 requires application of a finite shear stress to initiate flow, however TINCOL does not. Graph 2 illustrates the significantly different viscosities of the two pan release agents. The pan release agent of Example 1 has a constant viscosity at high shear rates but below a certain shear value, the viscosity changes rapidly.

These graphs clearly illustrates the difference between the pan release agent of the prior art and the pan release agent of the current invention which exhibits significantly improved adherence to the sides of dough pans.

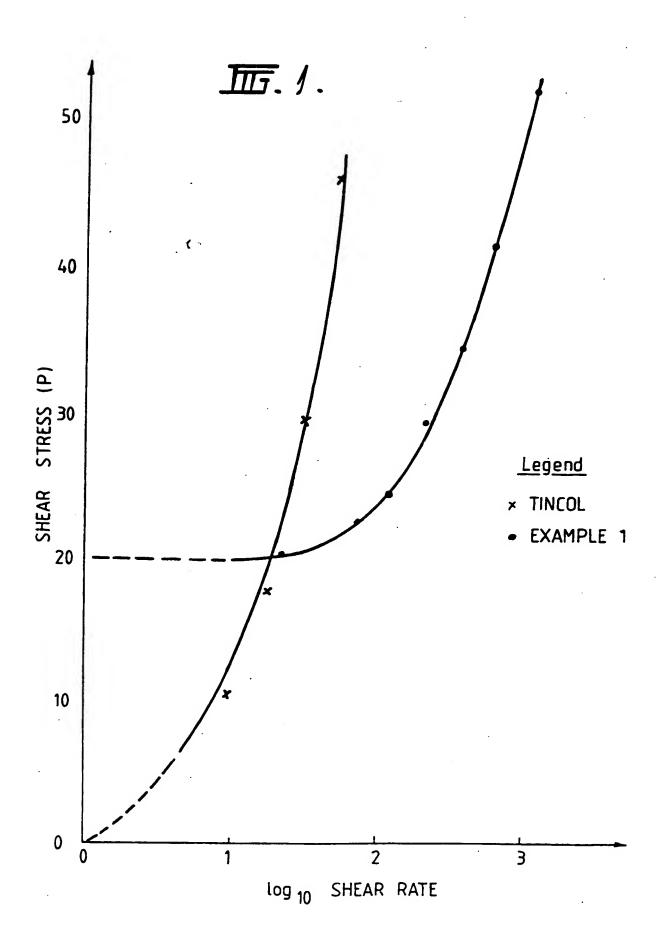
While the invention has been explained in relation to its preferred embodiments it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

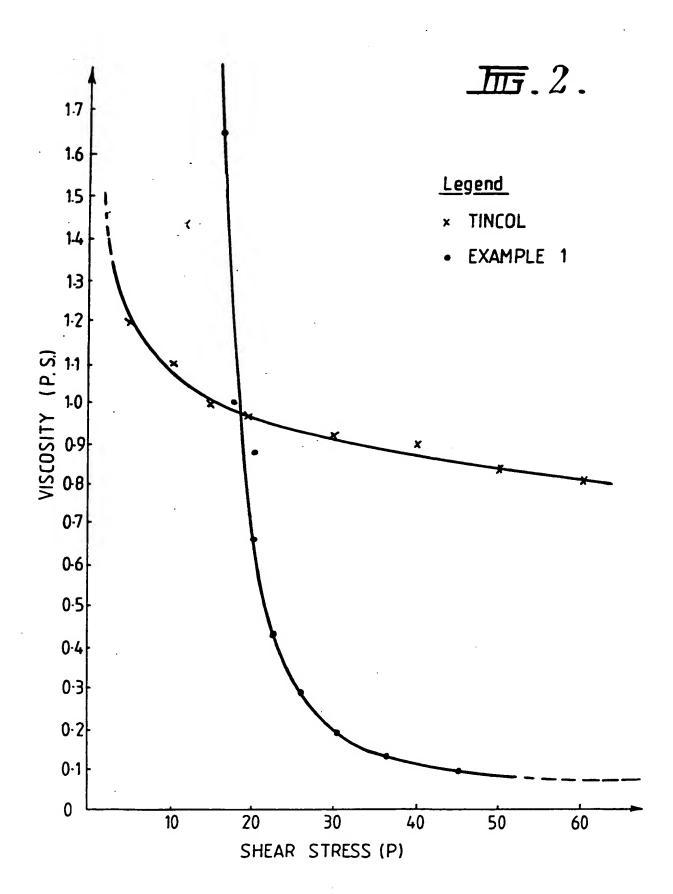
The claims defining the invention are as follows;

- 1. A fluid pan release agent comprising an emulsion comprising at least one oil, an aqueous phase and at least one emulsifier, wherein the mass ratio of aqueous phase:oil:emulsifier is from 75 to 90 for the aqueous phase, from 3 to 10 for the oil phase and from 1 to 12 for the emulsifier.
- A fluid pan release agent according to claim 1 wherein said fluid pan release agent exhibits non-Newtonian flow characteristics.
- A fluid pan release agent comprising at least one oil, an aqueous phase and at least one emulsifier wherein said fluid agent exhibits non-Newtonian flow characteristics.
- 4. A fluid pan release agent comprising at least one oil, an aqueous phase and at least one emulsifier wherein said fluid agent exhibits Bingham plastic flow and thixotropic flow characteristics.
- 5. A fluid pan release agent according to claim 3 wherein the mass ratio of aqueous phase:oil:emulsifier is from 75 to 90 for the aqueous phase, from 3 to 10 for the oil phase and from 1 to 12 for the emulsifier.
- 6. A fluid pan release agent according to any of claims 1, 2, 3 or 5 wherein said fluid pan release agent exhibits Bingham plastic flow and thixotropic flow characteristics.
- 7. A fluid pan release agent according to claim 6 wherein said pan release agent also comprises at least one preservative.
- 8. A fluid pan release agent according to claims 6 or 7 wherein said pan releas agent may be removed from a surface by application of water.

- 9. A fluid pan release agent according to claim 1 wherein said fluid pan release agent exhibits non-Newtonian flow characteristics which permit it to flow r adily und r applied pressur but which restrict its flow at atmospheric pressure.
- 10. A fluid pan release agent according to any of the preceding claims wherein said emulsifier is chosen from the group comprising monoglycerides and di-glycerides of fat forming fatty acids and monostearates, mono-stearates, mono-oleate derivatives and mixtures thereof.
- 11. A fluid pan release agent according to claim 10 comprising glycerol mono-oleate, sorbitan mono-stearate and polyoxyethylene sorbitan mono-stearate.
- 12. A fluid pan release agent according to claim 10 comprising glycerol mono-stearate, sorbitan mono-stearate and polyoxyethylene mono-oleate.
- 13. A fluid pan release agent according to any of the preceding claims wherein said oil phase is chosen from the group comprising liquid vegetable oils, animal fats and mixtures thereof.
- 14. A fluid pan release agent according to claim 13 wherein said oil phase comprises oil chosen from the group comprising canola oil, sunflower oil, soya oil, palm oil and mixtures thereof.
- 15. A fluid pan release agent according to any of the preceding claims which further comprises one or more additives chosen from the group comprising sorbic acid, acetic acid, phosphoric acid, benzoic acid and propionic acid.

16. A fluid pan release agent substantially as herein described with reference to the examples and the figures.





A. Int. Cl. ⁵ A	CLASSIFICATION OF SUBJECT MATTER 21D 8/08; A23D 7/00; A23D 7/02		
According to	o International Patent Classification (IPC) r to bo	th national classification and IPC	
В.	FIELDS SEARCHED		•
	secumentation searched (classification system follow 8/08; A23D 3/00; A23D 5/00; A23D 7/00; A		
Documentati AU:IPC as	on searched other than minimum documentation to above	the extent that such documents are included	in the fields searched
DERWENT	in base consulted during the international search ($^{\circ}$: water or H_20 or aque: for A23D 3/00 and $^{\circ}$ S: (water or H_20 or aque:) and (oil and emuls	A23D 5/00	urch terms used)
C.	DOCUMENTS CONSIDERED TO BE RELEV	ANT	
Category	Citation of document, with indication, where	appropriate, of the relevant passages	Relevant to Claim No.
x	WO,A,92/21335 (KABI PHARMACIA AE see example 2	3) 10 December 1992 (10.12.92)	1-16
x	US 4547388 (STROUSS L. ORAN) 15 Oct whole document	tober 1985 (15.10.85)	1-16
x	US 4339465 (STROUSS L. ORAN) 13 July whole document	y 1982 (13.07.82)	1-16
х	Derwent Abstract Accession No. 86-10576 (MOSC BREAD FACTORY) 7 October 19 abstract		1-16
	er documents are listed continuation of Box C.	See patent family annex	•
"A" docum not come carlie intern "L" docum or whanoth "O" docum exhib "P" docum	al categories of cited documents: ment defining the general state of the art which is onsidered to be of particular relevance of document but published on or after the lational filing date ment which may throw doubts on priority claim(s) lich is cited to establish the publication date of er citation or other special reason (as specified) ment referring to an oral disclosure, use, ition or other means ment published prior to the international filing date ter than the priority date claimed	considered to involve an document is taken alone document of particular r invention cannot be commended inventive step when the with one or more other:	te and not in conflict cited to understand the riving the invention relevance; the claimed sidered novel r cannot be inventive step when the relevance; the claimed sidered to involve an document is combined such documents, such ous to a person skilled in
	ctual completion of the international search 4 (23.06.94)	Date of mailing of the international search is 30 June 1994 (30	.06.94)
AUSTRALIZ PO BOX 200 WODEN AG AUSTRALIZ	CT 2606		ABLE COPY

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report	Patent Family Member			
WO,A, 92/21335	AU,A, 19101/92 PT,A, 100524	CA,A,2109611	NZ,A, 242697	
WO,A, 90/09107	AU,A, 51003/90	DK,A, 1382/91		
US,A, 4547388-	US,A, 4339465 EP,A, 67408 IN,A, 155645	CA,A, 1182830 HU,B, 186530 JP,A, 58000971	CH,A, 649996 IL,A, 65998 US,A, 4414400	
US,A, 4339465	US,A, 4547388 EP,A, 67408 IN,A, 155645	CA,A, 1182830 HU,B, 186530 JP,A, 58000971	CH,A, 649996 IL,A, 65998 US,A, 4414400	

END OF ANNEX

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT			
stegory	Citation of document, with indication, where appropriate of the relevant passages	Relevant to Claim No	
x	Patent Abstracts f Japan, C-1071, page 108, JP,A,05-030904 (OTSUKA SHOKUHIN K.K.) 9 February 1993 (09.02.93) abstract	·	
^		1-16	
x	WO,A,90/09107 (GRINDSTED PRODUCTS A/S) 23 August 1990 (23.08.90) whole document	3,4	
x	US 3906117 (ILIJA GAWRILOW) 16 September 1975 (16.09.75) whole document	3,4	
	Derwent Abstract Accession No. 86-228338, Class D21, JP,A,61-157340 (MORINAGA MILK K.K.), 17 July 1986 (17.07.86)		
X	abstract	3,4	
v	Derwent Abstract Accession No. 84-245868, Class D11 (D13), JP,A,59-146532 (UEDA SEIYU K.K.) 22 August 1984 (22.08.84)		
X	abstract	3,4	
x	Derwent Abstract Accession No. 83-817390, Class D13, JP,A, 58-170432 (SNOW BRAND MILK PRODUCTS) 7 October 1983 (07.10.93) abstract		
^	austratt ·	3,4	
	y The state of the		
	·		
	•		